Critical Angle of Non-Horizontal Surface for a Drop at Static Equilibrium

Submitted to:

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ChE 385M Surface Phenomena

Submitted by:

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Motivation:

Drops "sticking" to non-horizontal surfaces is a very common occurrence. One familiar example of this phenomena is a raindrop sticking to a car windshield. This project was inspired by an observation made while troubleshooting photolithography process issues in the manufacturing of microprocessors. The problem observed was that developer was not wetting parts of the wafer surface because the wafer was slightly tilted. This report specifically seeks to identify the angle of inclination of the solid surface at which a drop will begin to flow.

Issues:

This problem includes a phenomenon known as contact angle hysteresis which says that the contact angle is not unique. Very little is known or understood about this controversial phenomena and why it occurs. It is typically observed for moving contact lines that the contact angle of the advancing and receding contact lines depends on the speed at which the contact line is moving. Figure 1 shows typical experimental results of how the contact angle varies with the speed of a moving contact line.

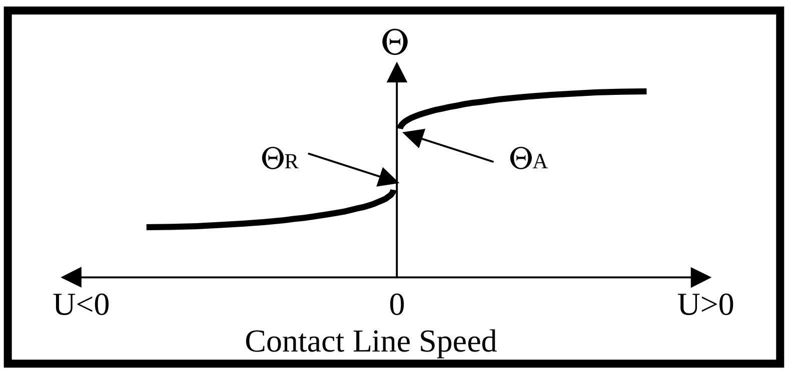

Figure 1: Example of Dynamic Contact Angle Measurements

The static contact angle Θ_S, i.e., the contact angle when the drop is at rest, then lies somewhere along the interval [Θ_R, Θ_A]. As it applies to this problem, hysteresis basically says that the contact angle is not constant along the contact line of the drop being modeled. See Figure 2.

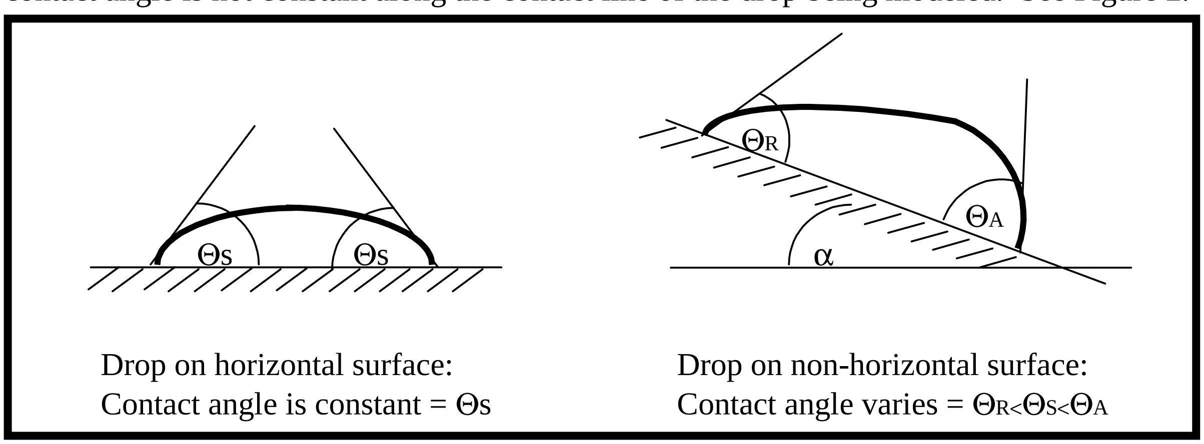

Figure 2: Example of Contact Angle Hysteresis

Model:

This problem will be modeled as a 3-dimensional drop at rest on a solid surface. The density of the drop, ρ, is assumed to be greater than the density of the surrounding gas. The critical static configuration is defined as the shape of the drop when the solid surface is tilted at the critical angle, $\alpha_{C.}$ Flow will begin at any angle greater than $\alpha_{C.}$ See Figure 3 for a diagram of the assumed model shape.

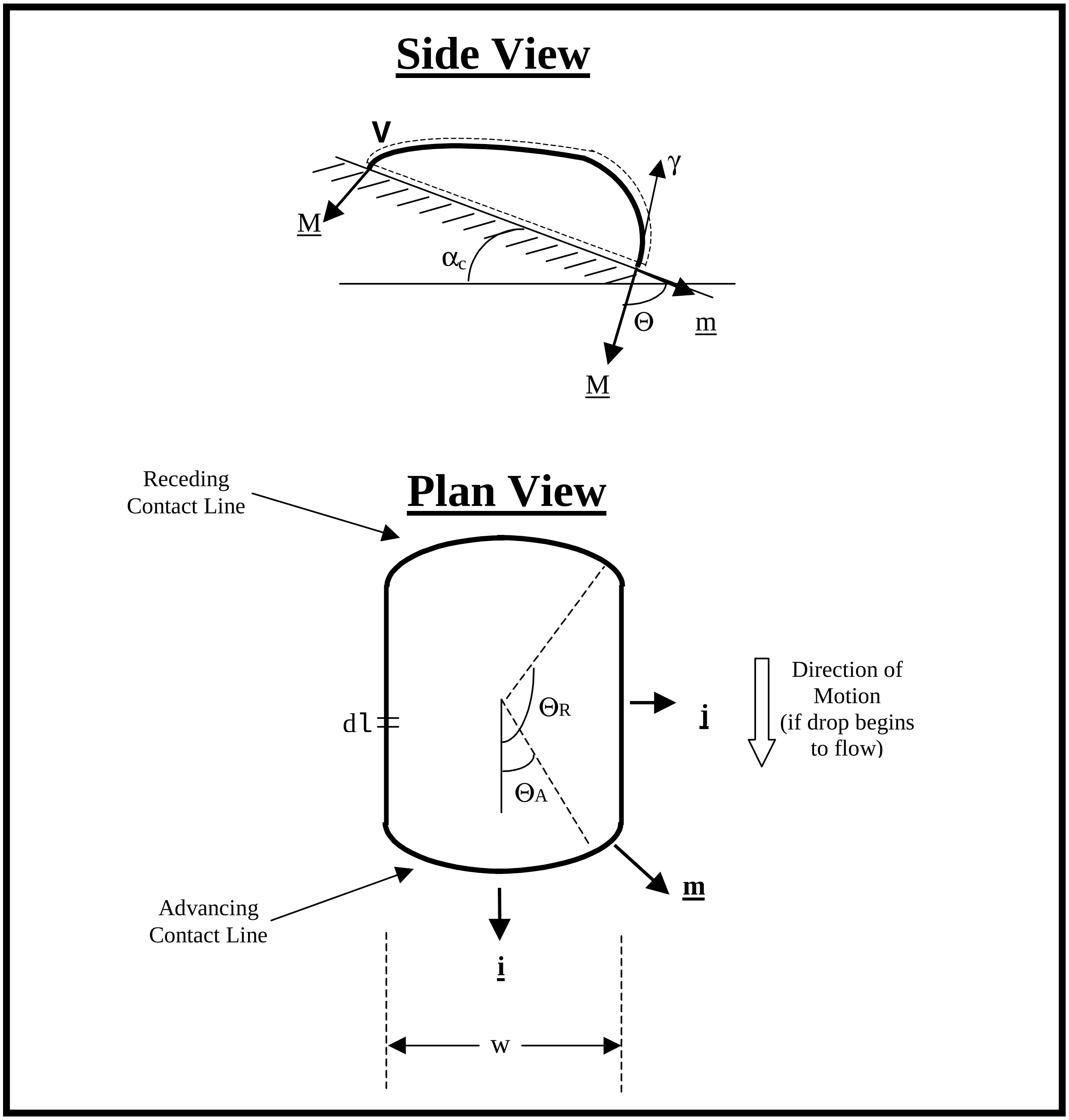

Figure 3: Drop at Critical Static Configuration.

Table 1 includes a list of variables and definitions as well as stating several assumptions needed to simplify this model and the resulting force balance.

Table 1. List of variables and definitions.

Variable	Definition
ρ	Density of drop
γ	Liquid to gas surface tension
α	Angle of Inclination of non-horizontal surface
α_C	Critical Angle of Inclination of non-horizontal surface
Θ	Contact angle, variable along contact line
Θ_A	Advancing contact angle, assumed constant along advancing contact line
Θ_R	Receding contact angle, assumed constant along receding contact line
V	Volume of drop, constant
w	Width of drop, assumed constant along the length of the drop
$d\mathtt{l}$	Length of differential segment of the contact line
g	Gravitational acceleration
$\underline{\mathrm{m}}$	Unit vector in the tangent plane to the solid surface, perpendicular to the contact line
$\underline{\mathrm{M}}$	Unit vector in the tangent plane of the liquid/gas interface, perpendicular to the vector tangent to the contact line
$\underline{\mathrm{i}}$	Unit vector in the direction of motion of the drop (if the drop begins to flow)
$\underline{\mathrm{j}}$	Unit vector perpendicular to the direction of motion of the drop (if the drop begins to flow) and parallel to the solid surface
V	Material body, bounded by dashed line -----
C	Location of contact line

Physics:

The physics governing this problem are simply the forces causing the drop to adhere to the surface (i.e., the surface tension forces) and the forces causing the drop to move steadily down the surface (i.e., the gravitational forces). When the drop is at rest in the critical static configuration, the force balance over the material body V will be

$$\Sigma \underline{\mathbf{F}} = 0 = \int_{C} [\gamma (\underline{\mathbf{M}} \bullet \underline{\mathbf{m}})\ \ \underline{\mathbf{m}}]\, d\mathtt{l} \quad + \rho\, V\, g \sin(\alpha_C)\ \underline{\mathbf{i}} \qquad (1)$$

This force balance incorporates the contact angle by using the definition of an angle, Θ, between two unit vectors.

$$\cos \Theta = \underline{\mathbf{M}} \bullet \underline{\mathbf{m}} \qquad (2)$$

With hysteresis, the contact angle varies along the contact line. The varying contact angle incorporates all the physical and chemical factors that cause the drop to adhere to the surface. These factors can include solid/liquid and solid/gas surface tensions, roughness of the solid surface, etc. The net surface tension force is the sum of all the forces along the length of the whole contact line, C, and is given by the integral term in equation (1).

The integral can be broken into 4 parts: the advancing and receding portions, and the two symmetrical straight-line portions on each side of the drop. Since this problem is only concerned with the forces acting in the "uphill" and "downhill" directions, Equation (1) can be dotted with unit vector $\underline{\mathbf{i}}$. Equation (1) then simplifies to

$$0 = \gamma \cos\Theta_A \int_{C_A} \underline{\mathbf{m}} \bullet \underline{\mathbf{i}}\, dl \quad + \gamma \cos\Theta_R \int_{C_R} \underline{\mathbf{m}} \bullet \underline{\mathbf{i}}\, dl \quad + \rho V g \sin(\alpha_C) \quad (3)$$

Integration over the width of the drop will yield the following result:

$$\rho\, g\, V \sin(\alpha_C) = \gamma\, w\, (\cos \Theta_R - \cos \Theta_A) \qquad (4)$$

Therefore, flow will begin for any angle, α, greater than α_C where α_C is given by

$$\alpha_C = \sin^{-1}\left[\frac{\gamma\, w\, (\cos \Theta_R - \cos \Theta_A)}{\rho\, g\, V}\right] \qquad (5)$$

See Appendix A for the detailed calculations needed for this derivation.

Results and Conclusions:

Equation (5) is a very simple calculation if all the quantities involved are known. However, this is not the case. Density, acceleration due to gravity, drop volume, and liquid/gas surface tension are all values easily obtained. The advancing and receding contact angles are only available from experimental data, and there is some controversy regarding the validity of the known experimental values. With this model, the width of the drop is unknown. However, a reasonable approximation of drop width may provide a valuable estimate of the critical angle for many practical purposes.

Further work on determining the critical static configuration is given in Reference 1.

References:

1. Dussan, E.B., and Robert Tao-Ping Chow. On the ability of drops or bubbles to stick to non-horizontal surfaces of solids. *J. Fluid Mech.* Vol. 137, pg 1-29. (1983)
2. Dussan, E.B. On the Spreading of Liquids on Solid Surfaces: Static and Dynamic Contact Lines. *Ann. Rev. Fluid Mech.* 1979, 11: 371-400.

Appendix A

Begin with a force balance on the material body of the drop, $\mathcal{V}$.

$$\Sigma \underline{F} = 0 = \int_{\ell} \gamma (\underline{M} \cdot \underline{m}) \underline{m} \, d\ell + m g \sin(\alpha_c) \underline{i} \qquad \text{(A1)}$$

Where m = mass of the drop = ρV

$$\Sigma \underline{F} = 0 = \int_{\ell} \gamma (\underline{M} \cdot \underline{m}) \underline{m} \, d\ell + \rho V g \sin(\alpha_c) \underline{i} \qquad \text{(A2)}$$

Equation (A1) incorporates the contact angle, θ, as it varies along the length of the contact line by using the following definition:

$$\cos \theta = \frac{\underline{M} \cdot \underline{m}}{\|\underline{M}\| \, \|\underline{m}\|} = \underline{M} \cdot \underline{m} \qquad \text{(A3)}$$

Where θ is the angle between the two unit vectors.

Since only the forces acting in the "uphill" or "downhill" directions are desired, equation (A2) can be dotted with $\underline{i}$ to obtain

$$\Sigma F = 0 = \int_{\ell} \gamma (\underline{M} \cdot \underline{m}) \underline{m} \cdot \underline{i} \, d\ell + \rho V g \sin(\alpha_c) \qquad \text{(A4)}$$

Appendix A

To simplify equation (A4), the integral can be broken into four parts.

$$\int_{\ell} \gamma(\underline{M}\cdot\underline{m})\underline{m}\cdot\underline{i}\, d\ell = \int_{\ell_A} \gamma \cos\theta_A\, \underline{m}\cdot\underline{i}\, d\ell + \int_{\ell_R} \gamma \cos\theta_R\, \underline{m}\cdot\underline{i}\, d\ell + \int_{\ell_{\text{left vertical}}} \gamma(\underline{M}\cdot\underline{m})\underline{m}\cdot\underline{i}\, d\ell + \int_{\ell_{\text{right vertical}}} \gamma(\underline{M}\cdot\underline{m})\underline{m}\cdot i\, d\ell \qquad (A5)$$

Due to symmetry, the j components of the integral (i.e., the left and right vertical parts) must be zero.

The first two parts of the integral represent the advancing and receding portions of the contact line, over which $\underline{M}\cdot\underline{m} = \cos\theta_A$ and $\cos\theta_R$, respectively. The advancing and receding contact angles are assumed to be constant over the advancing and receding contact lines.

Equation (A5) thus simplifies to

$$\int_{\ell} \gamma(\underline{M}\cdot\underline{m})\underline{m}\cdot\underline{i}\, d\ell = \gamma\left[\cos\theta_A \int_{\ell_A} \underline{m}\cdot\underline{i}\, d\ell + \cos\theta_R \int_{\ell_R} \underline{m}\cdot\underline{i}\, d\ell\right] \qquad (A6)$$

Since $\underline{m}$ and $\underline{i}$ are both unit vectors, (A6) becomes

$$\int_{\ell} \gamma(\underline{M}\cdot\underline{m})\underline{m}\cdot\underline{i}\, d\ell = \gamma\left[\cos\theta_A \int_{\ell_A} d\ell + \cos\theta_R \int_{\ell_R} d\ell\right] \qquad (A7)$$

Appendix A

Equation (A7) is then integrated over the contact line, moving in a counter clockwise direction

$$\int_{\ell} r(\underline{M}\cdot\underline{m})\underline{m}\cdot\underline{i}\, d\ell = \gamma\left[\cos\theta_A \int_0^W d\ell + \cos\theta_R \int_W^0 d\ell\right] \qquad \text{(A8)}$$

Evaluation of the integral gives

$$\int_{\ell} \gamma(\underline{M}\cdot\underline{m})\, \underline{m}\cdot\underline{i}\, d\ell = \gamma\left[\cos\theta_A (W) + \cos\theta_R(-W)\right] \qquad \text{(A9)}$$

Simplification of (A9) shows that

$$\int_{\ell} \gamma(\underline{M}\cdot\underline{m})\, \underline{m}\cdot\underline{i}\, d\ell = \gamma W(\cos\theta_A - \cos\theta_R) \qquad \text{(A10)}$$

Substituting (A10) back into (A4)

$$\Sigma F = 0 = \gamma W(\cos\theta_A - \cos\theta_R) + \rho V g \sin(\alpha_c) \qquad \text{(A11)}$$

or

$$\gamma W(\cos\theta_R - \cos\theta_A) = \rho V g \sin(\alpha_c) \qquad \text{(A12)}$$

Solving for α_c provides the final solution

$$\alpha_c = \sin^{-1}\left(\frac{\gamma W(\cos\theta_R - \cos\theta_A)}{\rho V g}\right) \qquad \text{(A13)}$$